# Magnetic order in the filled skutterudites $R\mathrm{Pt}_4\mathrm{Ge}_{12}$ ($R$ = Nd, Eu)

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**Abstract.** Rare-earth metal filled skutterudites $R\mathrm{Pt}_4\mathrm{Ge}_{12}$ with $R$=La-Nd, and Eu exhibit a variety of different ground states, e.g., conventional and unconventional superconductivity in $\mathrm{LaPt}_4\mathrm{Ge}_{12}$ and $\mathrm{PrPt}_4\mathrm{Ge}_{12}$, respectively, and intermediate valence behavior in $\mathrm{CePt}_4\mathrm{Ge}_{12}$. In this work we investigate the magnetic state of $\mathrm{NdPt}_4\mathrm{Ge}_{12}$ and $\mathrm{EuPt}_4\mathrm{Ge}_{12}$ by specific heat, dc-susceptibility and magnetization. $\mathrm{NdPt}_4\mathrm{Ge}_{12}$ shows two magnetic phase transitions at $T_{N1}$ = 0.67 K and $T_{N2}$ = 0.58 K, while $\mathrm{EuPt}_4\mathrm{Ge}_{12}$ displays a complex magnetic phase diagram below the magnetic ordering temperature of 1.78 K. The specific heat indicates that in $\mathrm{NdPt}_4\mathrm{Ge}_{12}$ the crystalline electric field (CEF) ground state of the $\mathrm{Nd}^{3+}$ is a quartet and that, as expected, in $\mathrm{EuPt}_4\mathrm{Ge}_{12}$ the $\mathrm{Eu}^{2+}$ state is fully degenerate.

## 1. Introduction

Filled skutterudites have become a topic of considerable interest with respect to basic and applied solid state sciences. This is particularly due to a variety of physical properties which can be intimately related to the underlying structural chemistry [1, 2, 3, 4, 5]. Their stoichiometry can be rationalized with the chemical formula $MT_4X_{12}$, with $M$ being an electropositive element like alkali, alkaline-earth, early rare-earth, actinide, or thallium metal, $T$ standing for a transition metal of the iron- or cobalt-group, and $X$ representing a pnictogen element as they are phosphorus, arsenic, or antimony. They all crystallize with the cubic $\mathrm{LaFe}_4\mathrm{P}_{12}$ [6] structure where cation $M$ stabilizes the $T_4X_{12}$ host structure. Recently it has been shown by us and others [7, 8] that the transition metal is not restricted to the iron or cobalt group, but can also be the noble metal platinum, which together with germanium acts as the framework forming elements stabilized by the alkaline-earth metals Sr and Ba. Moreover, we have discovered a whole new family of rare-earth metal ($R$) based filled skutterudites $R\mathrm{Pt}_4\mathrm{Ge}_{12}$ with $R$ = La-Nd, and Eu [8]. In turn, this series of compounds has been extended to actinide based $A\mathrm{Pt}_4\mathrm{Ge}_{12}$ ($A$= Th, U) phases [9, 10]. $M\mathrm{Pt}_4\mathrm{Ge}_{12}$ compounds ($M$ = Sr, Ba, La, Pr) are superconductors with $T_c$ up to 8.3 K [8]. $\mathrm{PrPt}_4\mathrm{Ge}_{12}$ is an unconventional superconductor with nodes in the superconducting energy gap [11]. Experimental and theoretical analysis of the electronic structure and chemical bonding revealed deep-lying Pt $5d$ states which only partially form covalent bands with the Ge $4p$ electrons. Consequently, the states at the Fermi level, which are relevant for superconductivity of these compounds, can be assigned to originate mainly from Ge $4p$ electrons [12]. Here, we report on the low-temperature magnetic properties of $R\mathrm{Pt}_4\mathrm{Ge}_{12}$ ($R$ = Nd, Eu) studied by specific heat, dc-susceptibility, and magnetization experiments.

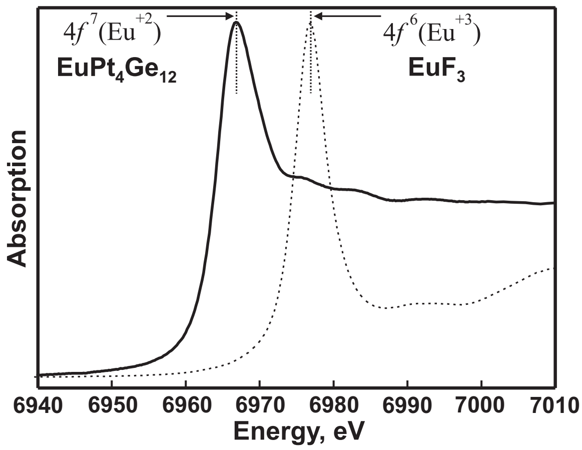


**Figure 1.** XAS of $EuPt_4Ge_{12}$ and $EuF_3$ at the Eu $L_{III}$ edge. The XAS were recorded at room temperature at the EXAFS beamline A1 of HASYLAB at DESY using the four-crystal mode of the Si(111) monochromator and determined in transmission mode using powdered samples ($\sim$10 mg) which were diluted with $B_4C$ and embedded in paraffin wax.

## 2. Experimental Details

Samples were synthesized as described elsewhere by arc-melting from the elements followed by annealing procedures [8]. We carried out low temperature (0.35K $\leq T \leq$ 10K) specific-heat ($C$) experiments using the $^3$He option of a PPMS (Quantum Design). The magnetization ($M$) in the temperature range 0.48K $\leq T \leq$ 1.9K was measured using a SQUID magnetometer (MPMS, Quantum Design) equipped with a $^3$He option (iQuantum). X-ray absorption spectroscopy at the Eu $L_{III}$ edge (6977 eV) was used to determine valence of this rare-earth metal in the structures of new filled skutterudite.

## 3. Experimental Results

### *3.1. $EuPt_4Ge_{12}$*

The X-ray absorption spectrum (XAS) for $EuPt_4Ge_{12}$ shown in Fig. 1 indicates that Eu is in the magnetic $4f^7$ ($Eu^{2+}$) configuration. No admixture of the $4f^6$ state is visible in the data. In $Eu^{2+}$ only the spin component contributes to the total angular momentum of the ground multiplet $^8S_{7/2}$ and, therefore, distinct crystalline electric field effects are expected to be absent.

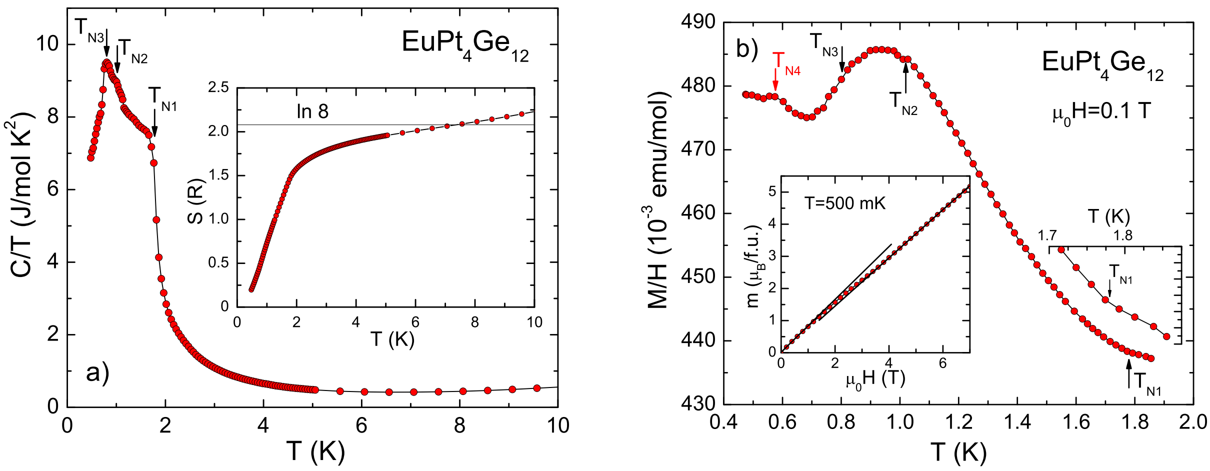


**Figure 2.** Specific heat as $C(T)/T$ (a) and dc-susceptibility $M(T)/H$ (b) of $EuPt_4Ge_{12}$. The arrows in (a) indicate the phase transitions. The inset of (a) shows the entropy $S(T)$. The black arrows in (b) correspond to the transition temperatures from specific heat, while the red arrow indicates an additional anomaly in $M(T)/H$. The inset of (b) presents $m(H)$ at $T \approx 500$ mK.

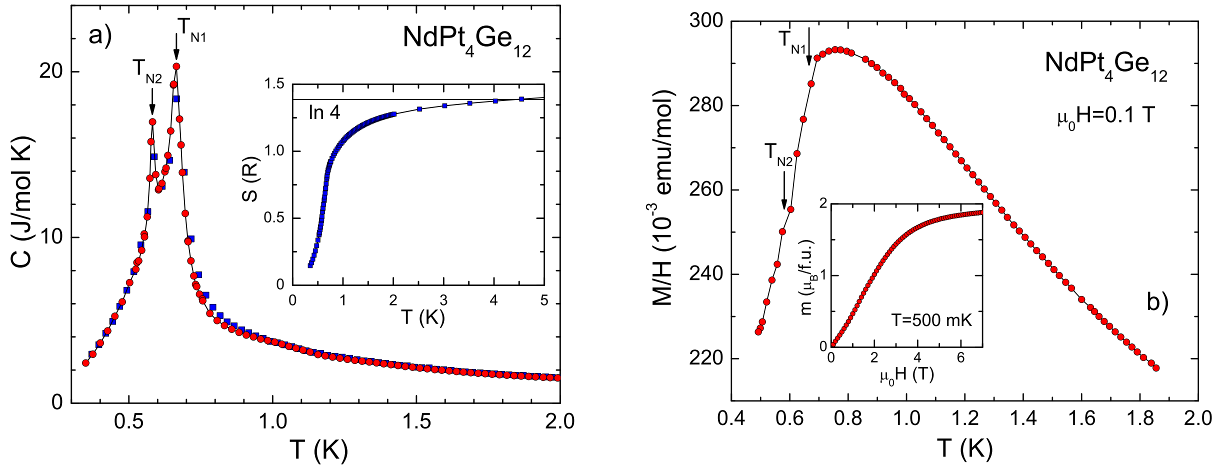


**Figure 3.** Specific heat as $C(T)/T$ (a) and dc-susceptibility $M(T)/H$ (b) of $\mathrm{NdPt_4Ge_{12}}$. For $C(T)/T$ the results from two different measurements are presented. The inset of (a) shows the entropy $S(T)$ determined form one of the $C(T)$ experiments. The inset of (b) displays $m(H)$ at $T \approx 500$ mK. The arrows in both panels correspond to the transition temperatures determined from specific heat.

Accordingly, a fully degenerated $J = 7/2$ ground state multiplet is anticipated. The specific heat, $C(T)/T$, of $\mathrm{EuPt_4Ge_{12}}$ is displayed in Fig. 2a. An analysis of $C(T)/T$ finds -as expected- a magnetic entropy of $R \ln 8$ (inset of Fig. 2a) at about 7 K.

$C(T)/T$ exhibits several anomalies at low temperatures. In contrast to previous works, reporting only one antiferromagnetic transition around $T_N \approx 1.7$, we can clearly identify at least three different anomalies, the first at $T_{N1} = 1.78$ K, at a slightly higher temperature than previously reported [8, 14], and at $T_{N2} = 1.03$ K and $T_{N3} = 0.8$ K. To further elucidate the nature of the phase transitions we conducted dc-susceptibility $(M(T)/T)$ measurements. The general shape of $M(T)/H$ is dominated by a strong increase upon decreasing temperature and a pronounced maximum just below 1 K. Below the maximum $M(T)/H$ decreases again and saturates toward lower temperatures. This overall shape is typical for antiferromagnetic ordering with a Néel temperature slightly below temperature where the maximum in $M(T)/H$ is observed. However, $C(T)$ exhibits a strong anomaly at a nearly twice as large temperature $T_{N1} = 1.78$ K. Surprisingly, the transition at $T_{N1}$ indicated by an arrow in Fig. 2b, is hardly visible in $M(T)/H$. Only in a magnification (right inset of Fig. 2b) a kink is visible at $T_{N1}$ hinting at a magnetic character of the transition. This transition has been also previously identified in resistivity data, while no indications for additional phase transitions at lower temperatures have been reported [14]. At $T_{N2}$ a small but clearly visible feature is evident in both, $C(T)/T$ and $M(T)/H$, while the most pronounced feature in $M(T)/H$ can be associated with $T_{N3}$. At $T_{N3}$ $C(T)/T$ shows a well developed peak. In $M(T)/H$ one additional phase transition can be recognized at $T_{N4}$. On a closer look a change in slope is visible in $C(T)/T$ at this temperature. The magnetization, $M(H)$, at $T \approx 0.5$ K is proportional to the magnetic field in the whole measurement range up to 7 T. We do not observe any tendency toward saturation since only $\approx 5\ \mu_\mathrm{B}$ are attained at our highest field. Only at about 2.5 T a tiny step hints at a subtle reorientation of the magnetic moments. Our results indicate complex magnetic ordering phenomena in $\mathrm{EuPt_4Ge_{12}}$ which ask for further investigations.

*3.2. $NdPt_4Ge_{12}$*

The specific heat, $C(T)/T$, of $NdPt_4Ge_{12}$ displayed in Fig. 3a shows two distinct peaks at $T_{N1} = 0.67$ K and $T_{N2} = 0.58$ K indicating two magnetic phase transitions. A previous resistivity study reported a rapid decrease of $\rho(T)$ below $\sim$0.7 K [13], which is in good agreement with $T_{N1}$. However, like in the case of $EuPt_4Ge_{12}$, no hint at the second phase transition has been observed in $\rho(T)$ [13]. The dc-susceptibility, $M(T)/T$, shows the typical temperature dependence of an antiferromagnetic material (see Fig. 3): with decreasing temperature $M(T)/T$ first continuously increases, exhibiting a maximum and then sharply drops on further decreasing temperature. As usually observed in an antiferromagnet the transition temperature ($T_{N1}$) coincides with the onset temperature of the drop in the susceptibility. At the second phase transition at $T_{N2}$ only a small kink, possibly indicating a reorientation of the magnetic moments, is evident in $M(T)/T$. The magnetization at $T \approx 0.5$ K deviates from a linear behavior above 4 T, but no saturation is reached up to 7 T. At 7 T a magnetic moment $m = 1.88$ $\mu_B$/f.u. is attained.

An analysis of the magnetic entropy points at a quartet ground state in the CEF level scheme. Already at $\sim$4 K the complete entropy corresponding to a quartet ground state, $R\ln 4$, is recovered, as displayed in the inset of Fig. 3a. In a CEF analysis of susceptibility and magnetization data of $NdPt_4Ge_{12}$ indeed a $\Gamma_{67}^{(2)}$ quartet ground state has been favored against a $\Gamma_5$ doublet [13]. In addition to our entropy analysis also the observed magnetic moment at 7 T and 0.5 K, $m = 1.88$ $\mu_B$/f.u., is significantly larger compared to the expected saturation moment in case of a $\Gamma_5$ doublet of 1.33 $\mu_B$/f.u.. Therefore, our data strongly supports the proposed $\Gamma_{67}^{(2)}$ quartet ground state [13].

## 4. Summary

In summary, $EuPt_4Ge_{12}$ and $NdPt_4Ge_{12}$ order magnetically below 1.78 K and 0.67 K, respectively. In $EuPt_4Ge_{12}$, Eu is in a stable magnetic $Eu^{2+}$ configuration. The analysis of the specific heat at low temperatures yields an entropy of $R\ln 8$ around 6 K consistent with a fully degenerate $J = 7/2$ multiplet. We could identify four anomalies in specific heat and dc-susceptibility evidencing a complex magnetic phase-diagram. At the lowest obtained temperature ($T \approx 0.5$ K) we do not observe any saturation of the magnetic moment in fields up to 7 T. $NdPt_4Ge_{12}$ shows one additional magnetic transition inside the magnetically ordered state which is possibly related to a re-arrangement of the magnetic moments. The analysis of the magnetic entropy points to a quartet CEF ground state. To clarify the nature of the magnetic order in $EuPt_4Ge_{12}$ and $NdPt_4Ge_{12}$ further studies on single crystals would be desirable.

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